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ScienceDirect
Catalysis Today 126 (2007) 359–368
CATALYSIS TODAY
www.elsevier.com/locate/cattod

# Design consideration of photocatalytic oxidation reactors using $TiO_2$-coated foam nickels for degrading indoor gaseous formaldehyde

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**Abstract**

In the design process of the photocatalytic oxidation (PCO) reactor using $TiO_2$-coated foam nickels, the optimum of catalyst film thickness, light intensity and flow velocity were considered. A model was developed to study the effect of catalyst film thickness on photocatalytic degradation of formaldehyde by a $TiO_2$-coated foam nickel at continuous flow mode. In this model, external mass transfer and internal molecule diffusion-reaction were considered. A first-order kinetics equation was used to account for the photocatalytic reaction. Two exponential equations were employed to describe the distribution of light intensities in foam nickels and catalyst films, respectively. Validated with experimental data, the model can be used to predict the optimal thickness of catalyst films. A method for determining appropriate light intensities was proposed and discussed. The appropriate light intensity can be obtained by giving a margin, regarded as an excess coefficient, to the light intensity calculated based on the assumption of complete use of excited electron–hole pairs. The excess coefficient needs to be determined experimentally. In addition, the optimal flow velocity of PCO reactors could be consistent with the required one by changing the windward area of foam nickels. Based on the theoretical analyses, a novel PCO reactor containing 15 parallel-connected cells was designed. Each reaction cell was composed of an UV lamp and a $TiO_2$-coated tubular foam nickel. The performance of the reactor was tested by degrading gaseous formaldehyde at an indoor concentration level. The results showed that the reactor had low pressure loss and good degradation capability.


*Keywords:* Photocatalysis; Reactor design; Air purification; Flow velocity; Catalyst film thickness; Light intensity

## 1. Introduction

Formaldehyde, as one of indoor volatile organic compounds (VOCs), exists extensively in modern building materials and household products. Its removal from indoor air is vital for improving human being's health due to a carcinogenic risk. The photocatalytic degradation of VOCs with the help of semiconductor catalyst has been shown to be a promising technology for air purification because a broad range of VOCs can be completely mineralized to environmentally harmless compounds such as $CO_2$ and $H_2O$ at room temperature and atmospheric pressure [1].

Although extensive studies on the reaction mechanism, the preparation and modification of catalysts and the photocatalytic degradation of VOCs have been done [2–4], the optimal design of photocatalytic oxidation (PCO) reactors is still a key unresolved issue in the application of photocatalysis technologies [5]. An efficient PCO reactor should have high degradation efficiency, high photon utilization and low pressure drop, which can be realized via the structural design and the parameter optimum of reactors. The factors that influence photocatalytic reaction rate include concentration, flow velocity, temperature, humidity, catalyst thickness and light intensity. Temperature has little influence on the reaction rate in the room temperature range due to low apparent activation energy of photocatalytic reaction. The photocatalytic reaction rate weakly depends on the relative humidity at low formaldehyde ppmv levels [4]. Concentration only influences the position of a reactor in a building or a air-conditioning system, which should be studied according to the specific building. Therefore, catalyst thickness, light intensity and flow velocity are optimized in this study.

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0920-5861/$ – see front matter © 2007 Published by Elsevier B.V.
doi:10.1016/j.cattod.2007.06.017

Most studies on the optimization of catalyst film thicknesses were done experimentally [6–8]. Chen et al. [9] presented a model to analyze the effect of catalyst film thickness on photocatalytic degradation rate. Chang et al. [10] established a kinetic model to predict the optimal thicknesses of catalyst films. Above two models are applicable to semi-batch or batch reactors, but they cannot be used at continuous flow mode because the concentration gradient exists in the flow direction.

It is well known that the light intensity is an essential factor influencing the reaction rate of VOCs and the utilization ratio of energy. Electron–hole recombination and interfacial electron transfer are second-order and first-order process, respectively. As a result, the recombination rate of electron–hole pairs increases relative to the transfer rate of interfacial electrons when the number of electron–hole pairs increases, which leads to a lower quantum efficiency [11]. Therefore, the recombination rate of electron–hole pairs should be decreased by using appropriate light intensities. Some radiation-field models [12–14] can predict the distribution of light intensities in reactors, but cannot predict appropriate light intensities.

In the present work, a model was presented to predict optimal catalyst film thicknesses for the degradation of indoor gaseous formaldehyde by a $TiO_2$-coated foam nickel at continuous flow mode. A method for determining appropriate light intensities was developed and discussed. A novel PCO reactor using $TiO_2$-coated foam nickels was designed and tested for the degradation of indoor gaseous formaldehyde at an indoor concentration level. This reactor is flexible enough to adapt to different air-processing systems under different air velocities by changing the windward area.

## 2. Design consideration

### 2.1. Model predicting optimal catalyst thicknesses

In this section, we established a model to predict the optimal thickness of catalysts coated on porous foam nickels at continuous flow mode.

#### 2.1.1. Mass transfer to the surface of catalysts from the bulk

Supposing that the flow through the foam nickel is plug flow, the equation of continuity for steady flow in the flow direction is:

$$u\frac{dC_b}{dz} + a_V k_m (C_b - C) = 0, \tag{1}$$

where $u$ is the face velocity of foam nickels (m/s), $z$ is the distance in the flow direction (m), $a_V$ is the specific surface area of foam nickels ($m^2_{Ni}/m^3$), $k_m$ is the mass transfer coefficient (m/s), $C_b$ is the bulk concentration of VOCs ($mol/m^3$), and $C$ is the concentration of VOCs on the catalyst surface ($mol/m^3$).

#### 2.1.2. Diffuse and reaction in catalyst films

Supposing that the diffusion of VOCs only exists in the direction of catalyst film thickness, the diffusion-reaction equation in catalyst films is described as follows:

$$\varepsilon_c D_e \frac{d^2C}{dx^2} - R = 0, \tag{2}$$

where $x$ is the distance in the direction of catalyst film thickness (m), $D_e$ is the effective diffusion coefficient of VOCs in catalyst films ($m^2/s$), $\varepsilon_c$ is the porosity of catalyst films, and $R$ is the intrinsic volumetric reaction rate of VOCs ($mol/m^3_c\,s$).

The Langmuir–Hinshelwood model has been widely used to evaluate the photocatalytic degradation rate [1]. Combining the UV light intensity, the volumetric reaction rate of VOCs can be written as follows:

$$R = k\left(\frac{\Delta I}{\Delta I'}\right)^n \frac{KC}{1+KC}, \tag{3}$$

where $k$ is the reaction rate constant under the volumetric absorbed light intensity $\Delta I'$ ($mol/m^3_c\,s$), $K$ is the adsorption equilibrium constant ($m^3_c/mol$), and $n$ is the reaction order of light intensity.

If $KC \ll 1$, the reaction is a first-order reaction with a constant reaction rate coefficient. Generally, the formaldehyde concentration in buildings including those exhibiting the 'sick building syndrome' are less than 2 ppmv [4,15,16]. For formaldehyde at an indoor level, first-order reaction rates can be observed [17,18], so Eq. (3) can be rewritten as

$$R = k'\left(\frac{\Delta I}{\Delta I'}\right)^n C, \tag{4}$$

where $k'$ is the apparent first-order volumetric reaction coefficient ($s^{-1}$).

#### 2.1.3. Distribution of light intensities

The exponential extinction form of light was introduced to describe the light intensity distribution in the flow direction and in the catalyst film [17,19]:

$$I_i = I_1 \exp[-\alpha_1 (i-1)\delta z], \quad i = 1, 2 \ldots l+1, \tag{5}$$

$$I_{i,j} = (I_i - I_{i+1}) \exp[-\alpha_2 (j-1)\delta x], \quad i = 1, 2 \ldots l \text{ and } j = 1, 2 \ldots p+1, \tag{6}$$

where $I_1$ is the total incident light intensity (W), $I_{i,j}$ is the light intensity at the $j$th interface of catalysts in the $i$th differential volume of foam nickels (W), $\delta z$ and $l$ are the thickness and the number of differential volume of foam nickels respectively, $\delta x$ and $p$ are the thickness and the number of differential volume of catalysts respectively, $\alpha_1$ and $\alpha_2$ are the optical attenuation coefficients in the flow direction and in the catalyst film ($m^{-1}$), respectively. The light intensity absorbed by the $j$th differential volume of catalyst in the $i$th differential volume of foam nickels can be expressed as:

$$\Delta I_{i,j} = I_{i,j} - I_{i,j+1} = \Delta I_{i,1} \exp[-\alpha_2 (j-1)\delta x], \quad i = 1, 2 \ldots l \text{ and } j = 1, 2 \ldots p, \tag{7}$$

*2.1.4. Boundary conditions*

The initial concentration of VOCs is equal to the inlet concentration:

$$C_b|_{z=0} = C_{in}. \tag{8}$$

There is no VOC passing through the catalyst/support interface, so:

$$\left.\frac{dC}{dx}\right|_{x=H} = 0. \tag{9}$$

At air/catalyst interface, the mass balance can be written as:

$$-D_{e,c}\left.\frac{dC}{dx}\right|_{x=0} = k_m(C_b - C). \tag{10}$$

Eqs. (1), (2) and (4–10) constitute the model for optimizing the thickness of catalyst films.

*2.1.5. Estimation and measurement of parameters*

There are six key parameters which need to be determined: the mass transfer coefficient from the bulk to the surface of catalysts, $k_m$, the effective diffusion coefficient in catalyst films, $D_e$, the optical attenuation coefficients of foam nickels and catalysts, $\alpha_1$ and $\alpha_2$, the first-order reaction rate constant, $k'$, and the reaction order of light intensity, $n$.

(a) *Mass transfer coefficient, $k_m$*: For porous media, the mass transfer coefficient can be calculated according to the following relationship among Sherwood number (*Sh*), Reynolds number (*Re*) and Schmidt number (*Sc*) [20]:

$$Sh = 1.17Re^{0.58}Sc^{1/3}, \tag{11}$$

where $Sc = \mu/\rho D$, $Re = \rho u d/\mu$, $Sh = k_m d/D$, $D$ is the diffusion coefficient in foam nickels ($m^2/s$), $d$ is the characteristic pore dimension of foam nickels (m), $\mu$ and $\rho$ are the viscosity and density of air, respectively.

(b) *Effective diffusion coefficient, $D_e$*: The effective diffusion coefficient of VOCs in catalyst films can be determined by the following formulas [20]:

$$D_e = D_{pore}\frac{\varepsilon_c}{\tau}, \tag{12}$$

$$\frac{1}{D_{pore}} = \frac{1}{D_A} + \frac{1}{D_K}, \tag{13}$$

where $\tau$ is the tortuosity of catalyst films, $\varepsilon_c$ is the porosity of catalyst films, $D_{pore}$ is the straight pore diffusion coefficient ($m^2/s$), and $D_K$ is the Knudsen diffusion coefficient ($m^2/s$).

The molecular diffusion coefficient can be estimated according to the semi-empirical Gilliland formula:

$$D_A = \frac{4.3559 \times 10^{-5}T^{3/2}}{P(V_A^{1/3} + V_B^{1/3})^2}\left(\frac{1}{M_A} + \frac{1}{M_B}\right)^{1/2}, \tag{14}$$

where $P$ is the pressure (Kpa), $T$ is the absolute temperature (K), $V_A$ and $V_B$ are the molar volumes of component A and B at boiling point, respectively ($cm^3$/mol), and $M_A$ and $M_B$ are the molar mass of component A and B, respectively.

The Knudsen diffusion coefficients of VOCs in catalyst films are calculated according to the following formula [21]:

$$D_K = \frac{1}{3}d_c\sqrt{\frac{8R_gT}{\pi M}}, \tag{15}$$

where $R_g$ is the molar gas constant (8.314 J/mol K), and $d_c$ is the characteristic pore diameter of catalyst films (m).

The porosity of catalyst can be determined according to the following equation:

$$V_c(1 - \varepsilon_c) = V_{Ni}(1 - \varepsilon'_{Ni}) - V_{Ni}(1 - \varepsilon_{Ni}) \tag{16}$$

where $\varepsilon_{Ni}$ and $\varepsilon'_{Ni}$ are the porosities of foam nickels before and after coating catalysts respectively, which can be measured by experiments. $V_{Ni}$ and $V_c$ are the volumes of foam nickels and catalysts, respectively. $V_c$ can be calculated according to the surface area of foam nickels and the film thickness of catalysts. For the tortuosity factor, $\sqrt{3}$ is typical for loose random structures [22].

(c) *Optical attenuation coefficients, $\alpha_1$ and $\alpha_2$*: The optical attenuation coefficients of foam nickels, $\alpha_1$, can be determined by measuring the transmitted UV light intensity under different foam nickel thicknesses. Sodergren et al. [23] developed a relationship between the optical attenuation coefficients of catalysts and the wavelength:

$$\alpha_2(\mu m^{-1}) = \exp[29 - 85\lambda(\mu m)] \tag{17}$$

But the use range of this formula is from 300 to 380 nm. The optical attenuation coefficient of catalysts can be obtained by investigating the optical absorption ratio of catalysts coated on a quartz glass under different film thicknesses and that of the quartz glass.

(d) *First-order volumetric reaction rate constant and reaction order of UV light intensity, $k'$ and $n$*: Considering that supports affect the characterization of catalysts, we used foam nickels coated with very thin $TiO_2$ films to obtain above parameters. The reaction order of UV light intensity can be obtained by investigating the reaction rate under different light intensities. After obtaining experimentally the total reaction mass, we can estimate the reaction mass in a differential volume of foam nickels. The total reaction mass can be expressed as:

$$q = \sum_{i=1}^{l} q_i = \sum_{i=1}^{l} q_1\left(\frac{\Delta I_i}{\Delta I_1}\right)^n = \sum_{i=1}^{l} q_1 \exp[-\alpha_2 n(i-1)\delta z],$$
$$i = 1, 2, \ldots l, \tag{18}$$

which is the sum of a constant proportional progression. The sum, $q$, and the common radio, $\exp(-\alpha_2 n\delta z)$, are known quantities, so the reaction mass in the first differential volume of foam nickels, namely, the first term

$q_0$, can be calculated. In the differential volume, the light intensity is considered to be uniform, so the reaction rate per unit catalyst volume can be calculated.

### 2.2. Method predicting appropriate light intensities

It is very essential to determine appropriate light intensities when a photocatalytic system is designed. The light intensity must meet degradation need of VOCs. In addition, excessive light intensity will reduce quantum efficiency and waste energy. In this section, we presented a method to determine appropriate light intensities for the photocatalytic degradation of indoor gaseous VOCs. An excess coefficient was defined based on the assumption of complete use of excited electron–hole pairs. The method employs the following assumptions:

(1) The excitation efficiency is 100%, namely, a photon with energy higher than the bandgap of the semiconductor can excite an electron–hole pair.
(2) Hydroxyl radical ($^{\bullet}$OH) is the primary oxidant in the process of VOCs degradation [24,25].
(3) The photocatalytic reaction proceeds at steady state.

Generally, the photocatalytic degradation of VOCs can be divided into the following four steps [26]:

$$TiO_2 + h\nu \rightarrow h^+ + e^- \quad \text{(R1)}$$

$$h^+ + H_2O \leftrightarrow {}^{\bullet}OH + H^+ \quad \text{(R2)}$$

$$h^+ + e^- \rightarrow \text{heat} \quad \text{(R3)}$$

$$VOC + {}^{\bullet}OH \rightarrow P \rightarrow \ldots \rightarrow CO_2 + H_2O \quad \text{(R4)}$$

When the recombination of electron–hole pairs does not occur, the flux of photons for attaining a certain reaction rate per unit area, $r$, can be expressed as:

$$G = \frac{sr}{k_1}, \ \text{Einstein/m}^2\,\text{s} \quad (19)$$

where $s$ is the number of $^{\bullet}$OH completely mineralizing a contaminant molecule, $k_1$ is the optical absorption coefficient.

The average energy of every photon is approximately equal to that of photon corresponding to main wavelength:

$$\bar{E} = E = h\nu = \frac{hc}{\lambda}, \quad (20)$$

where $\lambda$ is the main wavelength of light source, $c$ is the speed of light ($3 \times 10^8$ m/s), and $h$ is the Planck constant ($6.626 \times 10^{-34}$ J s).

The light intensity per unit reaction area can be expressed as:

$$I = 6.02 \times 10^{23} G\bar{E}, \quad (21)$$

where $6.02 \times 10^{23}E$ is the energy of an Einstein of photons.

By combining Eqs. (19–21), we obtain the following formula to calculate the light intensity:

$$I = \frac{6.02 \times 10^{23} srhc}{k_1 \lambda}, \ \text{W/m}^2 \quad (22)$$

Considering the electron–hole recombination, we can give a margin to the light intensity in Eq. (23), so the appropriate light intensity should be:

$$I_a = mI, \quad (23)$$

where $m$ can be considered as an excess coefficient.

After the reaction rates of VOCs under different light intensities is obtained experimentally, the values of $I$ can be calculated according to Eq. (22). The excess coefficient can be determined by investigating the radio of the used to the calculated light intensity and the increment of reaction rate.

### 2.3. Consideration on flow velocity

In heterogeneous catalytic reaction, mass transfer and surface reaction are two important factors controlling overall reaction rates [27]. Flow velocity affects mass transfer of bulk VOCs to the surface of catalysts and the resident time of VOCs on the surface of catalysts. At lower flow velocity, mass transfer controls the photocatalytic reaction process and the reaction rate increases with the increase of flow velocity. When the reaction process is free from mass transfer, the reaction rate will no longer increase. Therefore, there is an optimal flow velocity for a PCO reactor.

The determination of inlet or outlet flow velocity of a PCO reactor is influenced by many factors. For example, when a PCO reactor is applied to the centralized air-processing chamber in heating, ventilating and air-conditioning (HAVC) systems, the flow velocity is rather high for providing large air flux. We found that the once-through conversion of formaldehyde almost approached zero when the air flows vertically through a $TiO_2$-coated foam nickel at high flow velocities. For the used foam nickels, the optimal face velocity is less than the required flow velocity. However, the face velocity can be dropped to the optimal face velocity by increasing the windward area.

## 3. Experimental

### 3.1. Materials and catalysts

Precursor solution for $TiO_2$ films was prepared by sol–gel process. Tetrabutyl titante ($Ti(OBu)_4$, volume percent is 20.42%) and diethanolamine (DEA, volume percent is 5.76%) were dissolved in anhydrous ethanol (volume percent is 70.74%). After vigorous stirring for 1 h at room temperature, the mixture of deionized water (volume percent is 1.08%) and anhydrous ethanol (volume percent is 2.0%) was added dropwise into the solution under stirring. The resultant precursor solution was stirred for 2 h at room temperature, and then was sealed and placed in the dark for 24 h. Finally a uniform, stable, and transparent sol of $TiO_2$ was obtained.

Foam nickel wafer (porosity $\geq$ 95%, Ni $\geq$ 99.947 wt%) was used as catalyst supports. After treated by ultrasonic wave in ethanol to remove grease, foam nickels were washed with distilled water and dried at room temperature, then calcinated at 550 °C for 10 min in air. The specific surface area of the

calcinated foam nickels was 0.24 $m^2\,g^{-1}$. $TiO_2$ films were prepared by a dip-coating method. Foam nickels were dipped in the precursor solution and then rotated at high speed to form a wet gel film. After dried at room temperature for 12 h, the $TiO_2$-coated foam nickels were calcined at 550 °C for 45 min in air. Multiple coatings were carried out by repeating the same dip-coating and calcination procedures.

### 3.2. Characterization of $TiO_2$ films

The crystalline phase of the samples were characterized by an X-ray diffractometer (Bruker, D8 ADVANCE) with Cu Kα radiation (λ = 1.5405 Å). The accelerating voltage and the applied current were 40 kV and 40 mA, respectively. The X-ray diffraction (XRD) patterns of $TiO_2$ films coated on foam nickels with various coatings are showed in Fig. 1. For the bare foam nickel, only the peaks of Ni and NiO were detected. For the $TiO_2$-coated foam nickel, the diffraction peaks of $TiO_2$ (anatase) can be observed. In addition, the peaks of Ni and NiO were also detected since the X-ray penetrated through the very thin $TiO_2$ film to detect the supports.

The thickness of the catalyst film was estimated by the following formula [28]:

$$H = \frac{W}{a\rho_c}, \tag{24}$$

where $W$ is the loading of catalysts, $a$ is the surface area of foam nicekls, and $\rho_c$ is the density of catalysts. In our study, The $TiO_2$ loadings from one to three coatings were 21.3 g/$m^2$, 34.1 g/$m^2$ and 51.2 g/$m^2$, respectively. The surface area of foam nickels was 102.4 $m^2_{Ni}/m^2$ and the density of catalysts was 4 $g/cm^3_c$. The film thicknesses from one to three coatings were 52 nm, 83 nm and 125 nm, respectively.

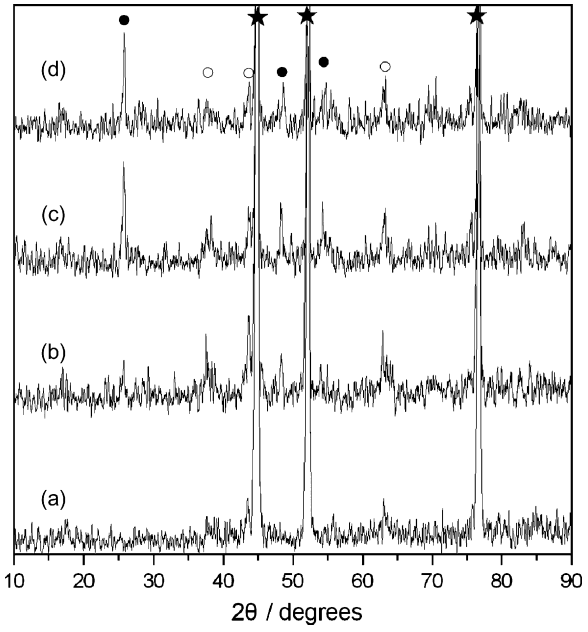


Fig. 1. XRD patterns of $TiO_2$ film on foam nickel calcined at 550 °C with various coatings (a) no coating (blank sample); (b) one coating; (c) two coatings; (d) three coatings. Symbols: (●) anatase $TiO_2$, (○) NiO, (★) Ni.

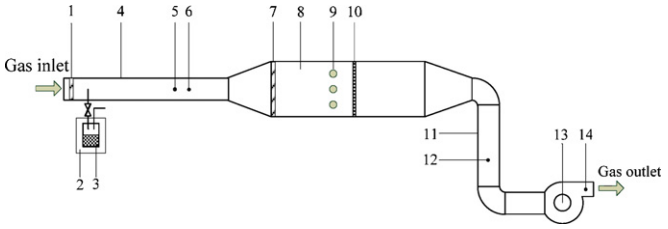


Fig. 2. Schematic diagram of the experimental apparatus for degrading gaseous formaldehyde (1) active carbon, (2) thermostatic saturator, (3) formaldehyde resolution, (4) mixing duct, (5) velocity measurement, (6) temperature and humidity measurement, (7) flow equalizer, (8) reaction chamber, (9) 254-nm UV lamp, (10) foam nickel, (11) steady-flow duct, (12) negative pressure measurement, (13) induced draft fan, (14) formaldehyde concentration measurement.

### 3.3. Experimental apparatus

The schematic diagram of the experimental apparatus for degrading gaseous formaldehyde is shown in Fig. 2. The reaction chamber was a simulated central air-conditioning chamber with the cross-sectional area of 0.4 m × 0.6 m. The mixing duct was long enough to obtain a uniform concentration field. In addition, a fully-developed velocity field was also obtained to reliably measure air state parameters and flow velocity. The flow equalizer could make the extended airflow pass through the reaction chamber uniformly. The $TiO_2$-coated foam nickel was vertically placed at the cross section of the reaction chamber. Three 15-W germicidal lamps emitting 254-nm UV were located in front of the foam nickel for attaining uniform light intensities.

The generation dose of gaseous formaldehyde was controlled by a thermostatic saturator and a valve. The concentration of formaldehyde was determined by a Formaldemeter PPM (PPM Technology Ltd., England). Flow velocity was adjusted by a variable-frequency induced fan at the outlet of experimental apparatus and was detected by a hot-wire anemometer RHAT-301 in the mixing duct (The flow velocity in the reaction chamber was used in the following discussions). Temperature and humidity was measured by a WS508/D digital thermometer. Light intensity was adjusted by changing the distance between the UV lamp and the foam Nickel and was measured by a UV-B digital radiometer. The optical absorption ratio of catalyst films was measured by a TU-1901 spectrophotometer (Beijing Purkinje General Instrument Co. Ltd, China). The pressure drop was measured by a pressure inclination gauge. The experiments were carried out at the temperature of 18–22 °C and the relative humidity of 50–60%.

### 3.4. Experimental procedure

The indoor air filtered by active carbons was used as the carrier gas. The purified air was discharged into another room with open windows. The concentration of formaldehyde was measured at the outlet of the experimental apparatus before and after turning on UV lamps and after turning off UV lamps. The schematic diagram of experimental procedure is shown in Fig. 3. When the adsorption equilibrium was reached, the lamps

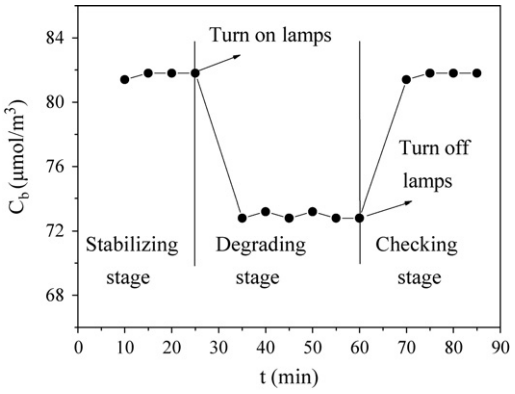


Fig. 3. Schematic diagram of experimental procedure.

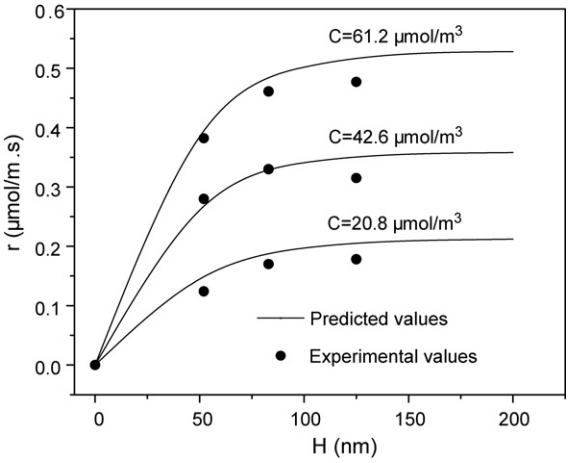


Fig. 4. Effect of the thickness of catalyst films on reaction rate of formaldehyde (Light intensity: 0.25 mW/cm$^2$, face velocity: 0.08 m/s).

were turned on. After the reaction reached the steady state, the lamps were turned off to investigate whether the outlet concentration was equal to the initial concentration. If the outlet concentration was equal to the initial concentration, the data were considered to be credible due to steady generation dose of formaldehyde. For the creditability of the data, the measurement procedure was carried out repeatedly.

## 4. Results and discussion

### 4.1. Optimal catalyst film thickness

A finite volume method was used to simultaneously solve Eqs. (1), (2), (4–7) with boundary condition Eqs. (8–10). The model parameters used to simulate the reaction rate of formaldehyde are listed in Table 1. The catalyst film with three coatings could completely absorb the UV light, so it was expected that the reaction rate would not increase with the increase of the number of coatings. Our experiments were carried out at no coating and one to three coatings. Comparisons of predicted and measured reaction rates of formaldehyde under different experimental conditions are shown in Table 2. Fig. 4 shows the effect of catalyst film thickness on the reaction rate of formaldehyde at 0.25 mW/cm$^2$ light intensity. A good correspondence between the predicted values and the experimental data was found. Therefore, the model can be used to predict the optimal catalyst film thickness at continuous flow mode.

As can be seen in Fig. 4, there was no photolysis. The by-product of formaldehyde photolysis is CO [4]. Though we did not measure the concentration of CO, a series of formaldehyde concentration measurement after UV lamps were turned on indicated that the photolysis of formaldehyde was negligible. Obee and Brown [4] found the concentration of CO increased linearly with the increase of light intensity from formaldehyde photolysis. For 3.3 ppmv formaldehyde, they observed 0.1 ppmv CO at 25 mW/cm$^2$ and no CO at 7 mW/cm$^2$. The light intensity used by us was 0.25 mW/cm$^2$. Thus, the possible reason of no photolysis was that the contact probability of formaldehyde with photons was very small at low concentrations and low light intensities. In Fig. 4, the reaction rate increased quickly firstly with the increase of thickness, which attributed to the further absorption of light intensity. And then the reaction rate reached a plateau due to the attenuation of light and the limit diffusion of formaldehyde in catalyst films. Fig. 5 shows the effects of the parameters ($D_e$, $k_m$, $\alpha_1$ and $\alpha_2$) on the optimal catalyst film thickness, $H_{opt}$. It could be seen that the effect of $k_m$, $\alpha_1$ and $D_e$ was weak, while the effect of $\alpha_2$ was strong. The value of $H_{opt}$ dropped quickly with the increase of the value of $\alpha_2$, and then reached a plateau.

In the present work, the optimal catalyst film thickness was about 80 nm, which was greatly different from that observed by Jung et al. [6] and Termakone et al. [7]. Jung et al. [6] found that the degradation of methylene blue by a $TiO_2$ film under an irradiation of 365-nm UV reached a maximum at about 5 μm. Termakone et al. [7] observed that the degradation of carbofuran by a thin-film $TiO_2$ catalyst under an irradiation

Table 1
Model parameters used to simulate the reaction rate of formaldehyde

| Symbol | Parameter description (unit) | Values |
|---|---|---|
| $\alpha_1$ | Optical attenuation coefficient of foam nickel (mm$^{-1}$) | 1.56 |
| $\alpha_2$ | Optical attenuation coefficient of catalyst (μm$^{-1}$) | 36.6 |
| $a_V$ | Specific surface area of supports ($m^2_{Ni}/m^3$) | 51200 |
| $k_m$ | Mass transfer coefficient (m/s) | 0.102 |
| $H'$ | Thickness of foam nickel (mm) | 2 |
| $k'$ | First-order volumetric reaction rate constant of formaldehyde (s$^{-1}$) | 3260 |
| $n$ | Reaction order of UV light intensity (1–4 W/m$^2$) | 0.52 |
| $D_e$ | Effective diffusion coefficient of formaldehyde in catalyst (m$^2$/s) | $2 \times 10^{-11}$ |

Table 2
Predicted and measured reaction rates of formaldehyde under different experimental conditions

| Test | $u$ (m/s) | $I$ (mW/cm$^2$) | $H$ (nm) | $C_b$ (μmol/m$^3$) | $r_m$ (μmol/m$^2$ s) | $r_P$ (μmol/m$^2$ s) | Δ (%) |
|---|---|---|---|---|---|---|---|
| 1 | 0.06 | 0.2 | 52 | 19.6 | 0.112 | 0.122 | 8.9 |
| 2 | 0.06 | 0.25 | 83 | 41.2 | 0.320 | 0.324 | 1.3 |
| 3 | 0.06 | 0.3 | 125 | 62.4 | 0.488 | 0.534 | 9.4 |
| 4 | 0.07 | 0.2 | 83 | 63.2 | 0.468 | 0.438 | 6.4 |
| 5 | 0.07 | 0.25 | 125 | 20.8 | 0.149 | 0.168 | 12.7 |
| 6 | 0.07 | 0.3 | 52 | 41.6 | 0.239 | 0.270 | 12.8 |
| 7 | 0.08 | 0.2 | 125 | 40.4 | 0.342 | 0.328 | 4.1 |
| 8 | 0.08 | 0.25 | 52 | 61.6 | 0.348 | 0.378 | 8.8 |
| 9 | 0.08 | 0.3 | 83 | 19.2 | 0.158 | 0.168 | 6.3 |

of 365-nm UV reached a maximum at about 6 μm. It is noted that the optical absorption situations by catalysts vary greatly with the wavelength. Cen et al. [29] found that there remained 84% of 365-nm light energy after penetrating a 1.4-μm $TiO_2$ film, but 254-nm light was absorbed intensely, and even could not penetrate a 140-nm $TiO_2$ film. The optical attenuation coefficient increases with the reduction of the wavelength [19,23]. The value of $\alpha_2$ measured by us for the 254-nm UV light was 36.6 μm$^{-1}$. In comparison, the value of $\alpha_2$ for 365-nm UV light was only 0.626 μm$^{-1}$[19]. Therefore, the strong effect of wavelength on the optical attenuation caused that the optimal catalyst film thickness was apparently different for different wavelengths.

### 4.2. Appropriate light intensity

The complete degradation of a formaldehyde molecule needs four $^{\bullet}$OH [2]. The appropriate light intensity for degrading gaseous formaldehyde was discussed by using the data of Obee [17] and our experimental data. In experiments of Obee [17], a glass-plate reactor with the area of 6.5 cm$^2$ was used to generate oxidation rate data. The light intensity was 0.33 mW/cm$^2$ (352 nm) and Reynolds number was 330. The optical absorption coefficient was not provided, and was estimated to be 0.92 according to the following formula:

$$k_1 = \frac{I_1 - I_1 \exp(-\alpha_2 H)}{I_1}. \tag{25}$$

Fig. 6 shows the reaction rate of formaldehyde under the light intensity of 0.33 mW/cm$^2$ in literature [17]. Table 3 shows the comparisons between the used by Obee [17] and the calculated light intensities ($m = 1$). When the concentration of formaldehyde increased from 85.89 to 490.8 μmol/m$^3$, the reaction rate had a small change (see Fig. 6) and the ratio of the used to the calculated light intensity ($m = 1$) was small (see Table 3). It was demonstrated the light intensity of

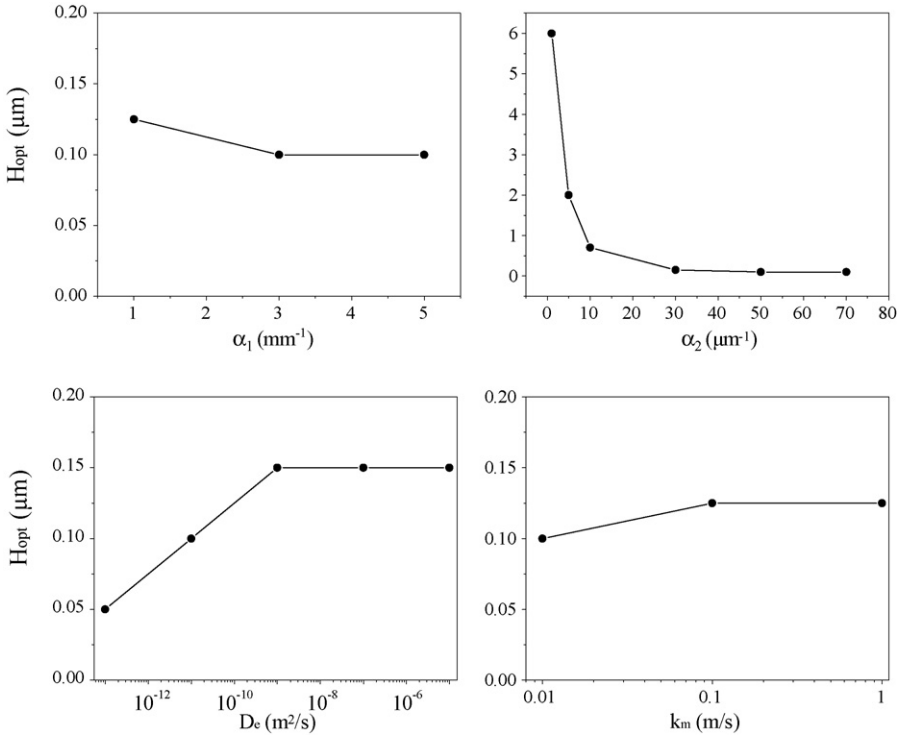


Fig. 5. Effects of $\alpha_1$, $\alpha_2$, $D_e$ and $k_m$ on $H_{opt}$.

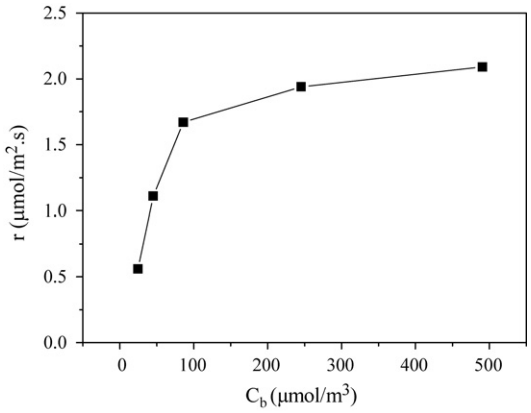


Fig. 6. Reaction rate of formaldehyde on glass plate reactor in literature [17].

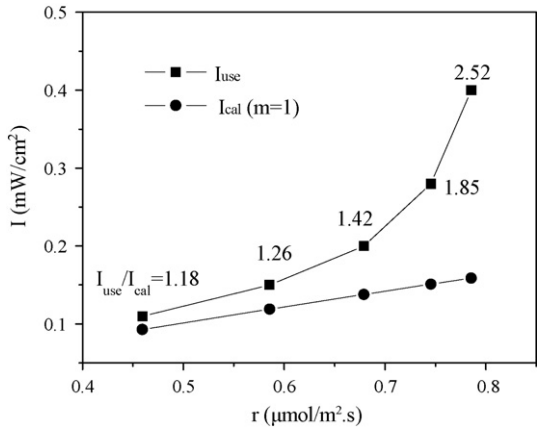


Fig. 7. Comparison between the calculated ($m = 1$) and the used light intensities (face velocity: 0.08 m/s).

0.33 mW/cm$^2$ had been fully utilized for formaldehyde of 85.89 μmol/m$^3$ and there was little electron–hole recombination. The reaction rate increased quickly with the increase of formaldehyde concentration from 24.54 to 85.89 μmol/m$^3$ (see Fig. 6), which indicated that the utilization ratio of 0.33 mW/cm$^2$ light intensity was enhanced markedly. When the concentration of formaldehyde was less than 85.89 μmol/m$^3$, the ratio was large (see Table 3). The excessive light intensity resulted in much electron–hole recombination. Therefore, the light intensity of 0.33 mW/cm$^2$ was high for formaldehyde concentration less than 85.89 μmol/m$^3$. We propose that lower light intensities should be used for the degradation of VOCs with lower concentrations, which can reduce the energy losses resulted from the electron–hole recombination. For formaldehyde of 85.89 μmol/m$^3$, which is approximately equal to 2 ppm, the light intensity of 0.33 mW/cm$^2$ is appropriate. The excess coefficient $m$ was 1.33.

Theoretically, different light intensities should be used for formaldehyde with different concentrations and can be attained by adjusting the input voltage of lamps, but the life length of lamps will be shortened. Therefore, the appropriate light intensity was determined according to the largest concentration taken as 2 ppmv in our experiments. The optimal catalyst thickness can adsorb incident light completely, so the optical absorption coefficient was estimated to be 0.93 according to the transmissivity of foam nickels. Fig. 7 shows the plots of the calculated light intensity ($m = 1$) and the used one versus the reaction rate of formaldehyde at the concentration of 81.8 μmol/m$^3$ (2 ppmv). With the increase of light intensity, the increment of reaction rate reduced, which indicated that the utilization ratio of light energy dropped. From the ratio of the used to the calculated light intensity ($m = 1$), we can also notice that the electron–hole recombination increased with the increase of light intensity. When the light intensity was greater than 0.2 mW/cm$^2$, the increase of the reaction rate was small, but the electron–hole recombination increased quickly. Accordingly, for obtaining good degradation performance and high photon utilization simultaneously, we considered the light intensity of 0.2 mW/cm$^2$ was appropriate for formaldehyde of 81.8 μmol/m$^3$. The excess coefficient was 1.42. It was noted that the light intensity had a great influence on the electron–hole recombination. When the ratio of the used to the calculated light intensity ($m = 1$) exceeded a certain value, the electron–hole recombination would increase quickly.

Table 3
Comparison between the light intensity used by Obee [17] and the calculated one ($m = 1$)

| Initial concentration (μmol/m$^3$) | Used light intensity $I_{use}$ (mW/cm$^2$) | Calculated light intensity $I_{cal}$ (mW/cm$^2$) | $I_{use}/I_{cal}$ |
|---|---|---|---|
| 24.54 | 0.33 | 0.084 | 3.93 |
| 44.99 | 0.33 | 0.166 | 1.99 |
| 85.89 | 0.33 | 0.249 | 1.33 |
| 245.4 | 0.33 | 0.290 | 1.14 |
| 490.8 | 0.33 | 0.312 | 1.06 |

### 4.3. Structural design of a PCO reactor

A novel PCO reactor containing 15 parallel-connected reaction cells was designed. The schematic diagram of the reactor is shown in Fig. 8. Each cell was composed of an UV lamp and a $TiO_2$-coated tubular foam nickel. The length and diameter of each cell were 0.44 m and 0.098 m, respectively.

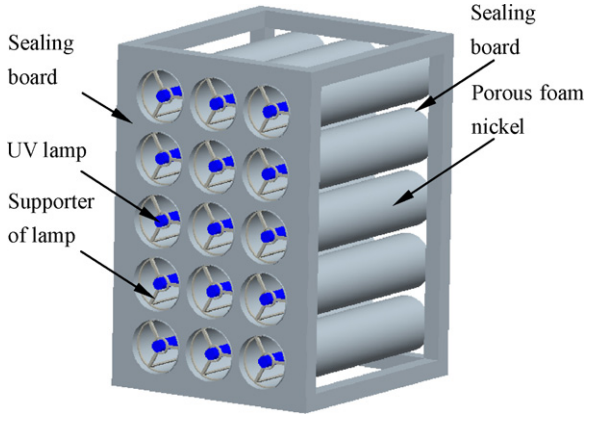


Fig. 8. Schematic diagram of the PCO reactor.

The UV lamp was placed in the center of each tubular foam nickel. This position can provide good irradiation. One end of each tubular foam nickel was sealed by a sealing board so that the air could enter each cell along the axial direction and then flow out through the holes of foam nickels along the radial direction. This kind of special configuration could have much larger reaction area on a finite cross section and reduce the face velocity of foam nickels. Therefore, the low pressure drop of the reactor and the relatively long resident time of VOCs could be obtained simultaneously. According to the analyses on the appropriate light intensity and the optimal catalyst thickness, the light intensity of 0.2 mW/cm$^2$ and the catalyst with two coatings were employed to investigate the performance of the reactor.

### 4.4. Performance investigation

The resistance of reactors, as an important design parameter, can influence the electrical energy consumption. However, little work has been done on the measurement of the resistance in literature. We measured the resistances of the reactor and a piece of foam nickel placed vertically in the cross section of the reaction chamber, respectively. The plot of the resistance versus the flow velocity is shown in Fig. 9. It was found that the method of decreasing the resistance by increasing the windward area was effective. When the flow velocity was less than 2 m/s, the resistance of the reactor was less than 21 Pa. The impact of the resistance on the performance of the fan in the HVAC system is negligible, so the additional driving apparatus is not needed.

The photolysis of formaldehyde in the $TiO_2$-uncoated photoreactor was investigated. A series of formaldehyde concentration measurement indicated that the photolysis of formaldehyde was negligible.

The once-flow conversions and reaction rates of formaldehyde under different concentrations and at 0.66 m/s are shown in Fig. 10. The reaction rate increased with the increase of formaldehyde concentration due to the increase of the contact probability of formaldehyde with $^{\bullet}$OH.

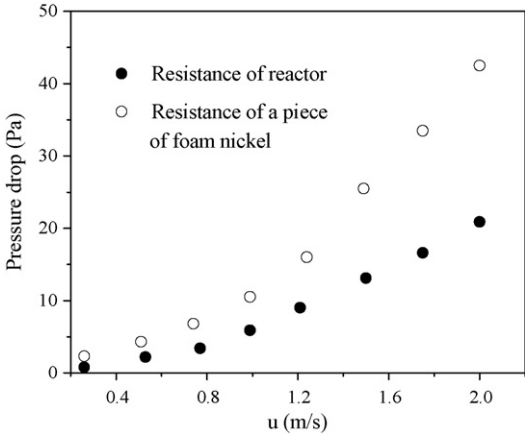


Fig. 9. Plots of the resistance of the reactor and that of a piece of foam nickel versus flow velocity.

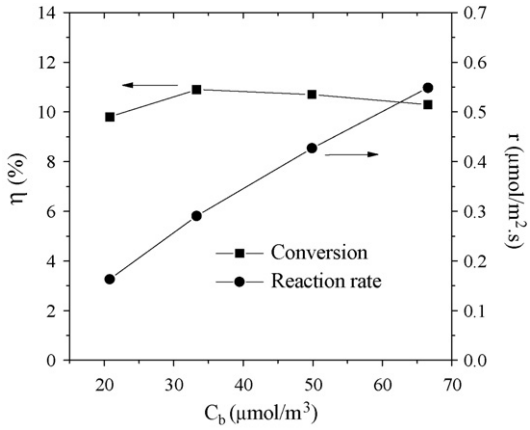


Fig. 10. Once-flow conversions and reaction rates of formaldehyde under different concentrations (Light intensity: 0.2 mW/cm$^2$, flow velocity: 0.66 m/s).

The once-flow conversions and reaction rates of formaldehyde under different flow velocities are shown in Fig. 11. The conversion decreased with the increase of flow velocity. The reaction rate increased when the flow velocity increased from 0.47 to 0.66 m/s and decreased when the flow velocity ranged from 0.66 to 0.94 m/s. When the flow velocity was larger than 0.66 m/s, the reaction rate was controlled by the surface reaction and the influence of the external mass transfer was negligible. The optimal flow velocity of the reactor was 0.66 m/s, which can be adjusted by changing the windward area. Therefore, this kind of configuration is flexible enough to adapt to different HVAC systems. It is interesting to note that there are two tendencies of reaction rate with the increase of flow velocity when the reaction rate is free from external mass transfer. Some authors observed that the reaction rate increased firstly and then dropped with the increase of flow velocity [30,31], while anothers observed that the reaction rate increase firstly and then reach a plateau [32]. The different tendencies resulted from the different resident time maybe. The complete degradation of VOCs to $CO_2$ and $H_2O$ needs certain reaction time. When the resident time of VOCs was too short, the reaction rate declined.

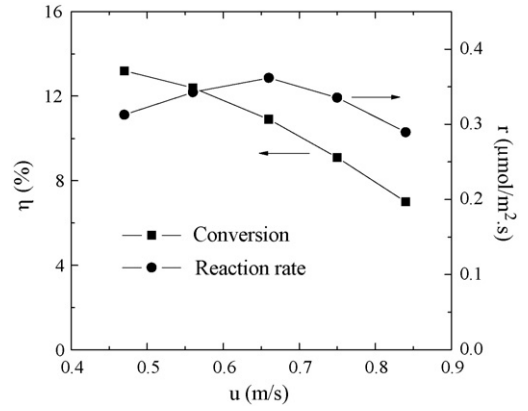


Fig. 11. Once-flow conversions and reaction rates of formaldehyde under different air velocities (Light intensity: 0.2 mW/cm$^2$, concentration: 41.6 μmol/m$^3$).

## 5. Conclusions

In the present work, a model was developed to predict the optimal film thickness based on the external mass transfer and internal molecule diffusion-reaction. The model was validated using the data of formaldehyde degradation. The simulation results showed that the reaction rate of formaldehyde increased firstly and then reached a plateau with the increase of the thickness of catalyst films. The analysis based on the proposed model showed that the optimal thickness of catalyst films was mainly influenced by optical attenuation coefficients in catalyst films. The optimal thickness of catalyst films was about 80 nm, which was very thin in comparison with that in literature due to strong absorption of 254-nm photons.

A method was proposed to determine appropriate light intensities for the photocatalytic degradation of indoor VOCs. The appropriate light intensity can be obtained by giving a margin, regarded as an excess coefficient, to the light intensity calculated based on the assumption of complete use of excited electron–hole pairs. The excess coefficient and the appropriate light intensity for degrading formaldehyde were determined according to the data obtained from literature and our experiments. For the $TiO_2$-coated glass plate, 0.33 mW/cm$^2$ light intensity (352-nm UV) was appropriate for formaldehyde of 2 ppm or so and the excess coefficient was 1.33. For the $TiO_2$-coated foam nickel, 0.2 mW/cm$^2$ light intensity (254-nm UV) was appropriate for formaldehyde of 2 ppm and the excess coefficient was 1.42. Maybe the excess coefficient is subjected to the restriction of the types of catalysts and reactors, which should be further investigated.

On the basis of the theoretical analyses, a novel PCO reactor containing 15 parallel-connected cells was designed. Each cell was composed of an UV lamp locating at the center of a $TiO_2$-coated tubular foam nickel. This kind of special configuration could have much larger reaction area on a finite cross section and reduce face velocity of foam nickels. Therefore, the configuration could be used at high flow velocity. At the same time, the low pressure drop of the reactor and the relatively long resident time of VOCs could be obtained. The photocatalytic performance of the reactor with the optimal catalyst film thickness and the appropriate light intensity was investigated by degradation of gaseous formaldehyde. The experimental results showed that the reactor have low pressure loss and good degradation capability. The maximum reaction rate occurred at 0.66 m/s. The optimal flow velocity can be adjusted by changing the windward area of the reactor.

## Acknowledgements

The study was supported by the Special Foundation of Nanometer Technology (No. 0552nm002), from Shanghai Municipal Science and Technology Commission (STCSM), China.

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